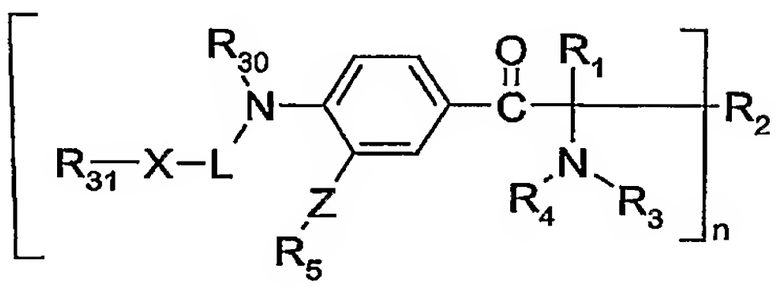
Claims

1. Photoinitiators of the formula I



I

wherein

n is 1 or 2;

L is a linker;

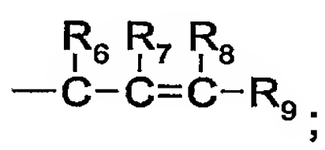
X is -O-, -S- or -NR_{32}-;

Z is a direct bond, -CH_2-, -O-, -S- or -NR_{10}-;

R_1 is

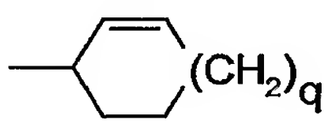
(a) linear or branched C_1-C_{12}-alkyl, which is unsubstituted or substituted by one or more of the groups C_1-C_4-alkyoxy, phenoxy, halogen or phenyl;

(b) a radical of the formula



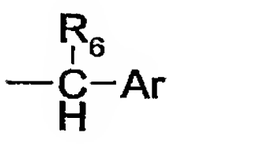
;

(c) a radical of the formula



where q is 0, 1, 2 or 3; or

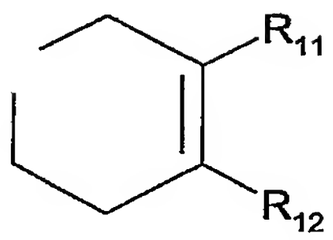
(d) a radical of the formula



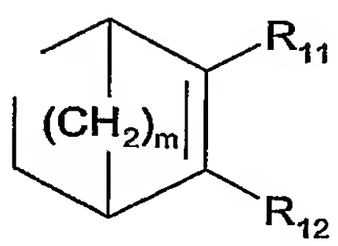
where Ar is phenyl, which is unsubstituted or substituted by one or more of the groups halogen, OH, NO_2, -N(R_{10})$_2$, C_1-C_{12}-alkyl, C_1-C_4-alkyl that is additionally substituted by OH, halogen, N(R_{10})$_2$, C_1-C_{12}-alkoxy, -COO(C_1-C_{18}-alkyl), -CO(OCH_2CH_2)$_n$$OCH_3$ or -OCO(C_1-C_4-alkyl); C_1-C_{12}-alkyoxy, C_1-C_4-alkyoxy that is additionally substituted by -COO(C_1-C_{18}-alkyl) or -CO(OCH_2CH_2)$_n$$OCH_3$; -OCO($C_1$-$C_4$-alkyl), C_1-C_8-alkylthio, phenoxy, -COO(C_1-C_{18}-alkyl), -CO(OCH_2CH_2)$_n$$OCH_3$, phenyl or benzoyl; where n is 1-20;

R_2 if n is 1, independently of R_1 has one of the meanings of R_1; or

R_1 together with R_2 forms a ring of the formula



or



where m is 1 or 2;

R_2 if n is 2, is a direct bond, C_2-C_{16}-alkylene, cyclohexylene, xylylene, dihydroxyxylylene, C_4-C_8-alkenediyl, C_6-C_{10}-alkadienediyl or dipentenediyl;

R_3 is hydrogen, C_1-C_{12}-alkyl, C_2-C_4-alkyl substituted by one or more of the groups hydroxy, C_1-C_4-alkoxy, -CN, -COO(C_1-C_4-alkyl); C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl or C_7-C_9-phenylalkyl;

R_4 is C_1-C_{12}-alkyl, C_2-C_4-alkyl substituted by one or more of the groups hydroxy, C_1-C_4-alkoxy, -CN, -COO(C_1-C_4-alkyl); C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, phenyl; or R_4 and R_2 together is C_1-C_7-alkylene, C_7-C_{10}-phenylalkylene, o-xylene, 2-butenylene or C_2-C_3-oxa- or azaalkylene; or R_4 and R_3 together is C_3-C_7-alkylene that may be interrupted by -O-, -S-, -CO- or -N($\mathbf{R_{13}}$)- and substituted by hydroxy, C_1-C_4-alkoxy or -COO(C_1-C_4-alkyl);

R_5 is hydrogen or C_1-C_4-alkyl; or R_5 together with R_{30} is C_1-C_2-alkylene;

R_6 is hydrogen, C_1-C_8-alkyl or phenyl;

R_7, R_8 and R_9 independently of each other are hydrogen or C_1-C_4-alkyl, or R_7 and R_8 together are C_3-C_7-alkylene;

R_{10} is hydrogen, C_1-C_8-alkyl, C_3-C_5-alkenyl, C_7-C_9-phenlyalkyl, C_1-C_4-hydroxyalkyl or phenyl;

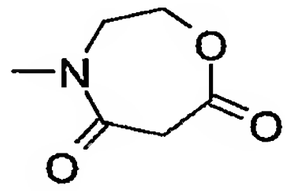
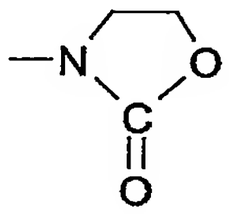
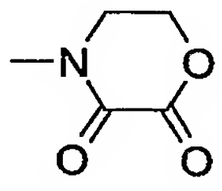
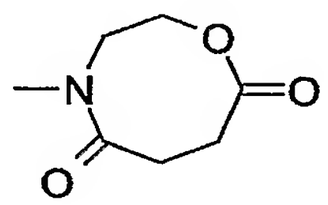
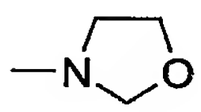
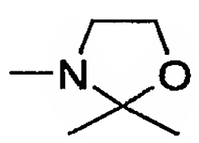
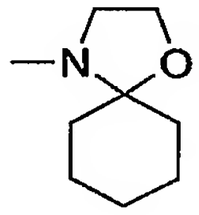
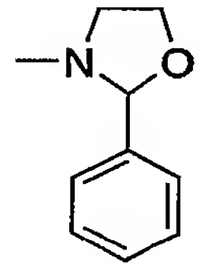
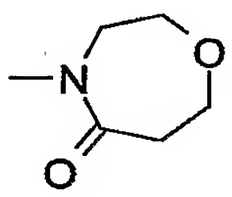
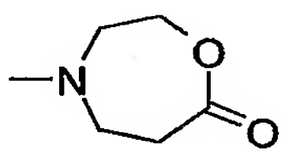
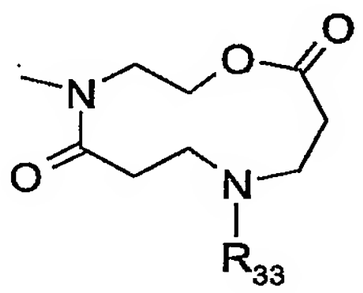
R_{11} and R_{12} independently of each other are hydrogen or C_1-C_4-alkyl, or R_{11} and R_{12} together are C_3-C_7-alkylene;

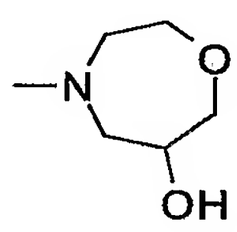
R_{13} is hydrogen, C_1-C_{12}-alkyl, which may be interrupted by one or more -O- or C_3-C_5-alkenyl, C_7-C_9-phenylalkyl, C_1-C_4-hydroxyalkyl, -CH_2CH_2CN, -CH_2CH_2COO(C_1-C_4-alkyl), C_2-C_8-alkanoyl, or benzoyl;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{18}-alkyl or C_1-C_{18}-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), -CN and/or -COO(C_1-C_4-alkyl); C_3-C_{18}-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl substituted by C_1-C_4-alkoxy, -$N\mathbf{R_{33}R_{34}}$, -$S\mathbf{R_{35}}$, -COOH or -COO(C_1-C_4-alkyl); or benzoyl or norbornenoyl substituted by hydroxy, or C_3-C_5-alkenoyl, -SO_2-(C_1-C_{12}-alkyl) or –SO_2-(C_1-C_{12}-alkylphenyl); or -CO-NH-C_1-C_{12}-alkyl or -CO-NH-(C_0-C_{12}-Alkylen)-N=C=O optionally interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene,

cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-isocyanatohexyl)-[1,3,5]triazinan-2,4,6-trion-1,3-diyl; or

R_{30} and R_{31} together with the group –N-L-X form cyclic structures selected from



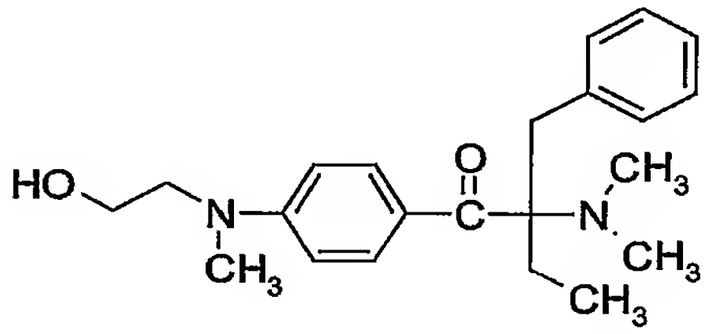
R_{32} is hydrogen, C_1-C_{18}-alkyl or C_1-C_{18}-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), -CN and/or -COO(C_1-C_4-alkyl); C_3-C_{18}-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, C_2-C_{18}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{18}-alkanoyl benzoyl or norbornenoyl substituted by hydroxy, C_1-C_4-alkoxy, -$NR_{33}R_{34}$, -SR_{35}, -COOH or -COO(C_1-C_4-alkyl); or C_3-C_5-alkenoyl, -SO_2-(C_1-C_{12}-alkyl) or –SO_2-(C_1-C_{12}-alkylphenyl); or -CO-NH-C_1-C_{12}-alkyl or -CO-NH-(C_0-C_{12}-Alkylen)-N=C=O optionally interrupted by one or two phenylene, methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-isocyanatohexyl)-biuret-1,5-diyl or 5-(6-isocyanatohexyl)-[1,3,5]triazinan-2,4,6-trion-1,3-diyl;

R_{33} and R_{34} independently of one another are hydrogen, C_1-C_{12}-alkyl, C_2-C_4-hydroxy-alkyl, C_3-C_{10}-alkoxyalkyl, C_3-C_5-alkenyl, C_5-C_{12}-cycloalkyl, C_7-C_9-phenylalkyl, phenyl, C_2-C_{18}-alkanoyl or benzoyl; or R_{33} and R_{34} together are C_2-C_8-alkylene optionally interrupted by -O-, -S- or -NR_{36}- , or are C_2-C_8-alkylene optionally substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or -COO(C_1-C_4-alkyl);

R_{35} is C_1-C_{18}-alkyl, hydroxyethyl, 2,3-dihydroxypropyl, cyclohexyl, benzyl, phenyl, C_1-C_{12}-alkylphenyl, -CH_2-COO(C_1-C_{18}-alkyl), -CH_2CH_2-COO(C_1-C_{18}-alkyl) or -CH(CH_3)-COO(C_1-C_{18}-alkyl);

R_{36} is hydrogen, C_1-C_{12}-alkyl optionally interrupted by one or more no adjacent –O-atoms, C_3-C_5-alkenyl, C_7-C_9-phenylalkyl, C_1-C_4-hydroxyalkyl, -CH_2CH_2CN, -CH_2CH_2COO(C_1-C_4-alkyl), C_2-C_{12}-alkanoyl or benzoyl;

with the proviso that the following compounds are excluded: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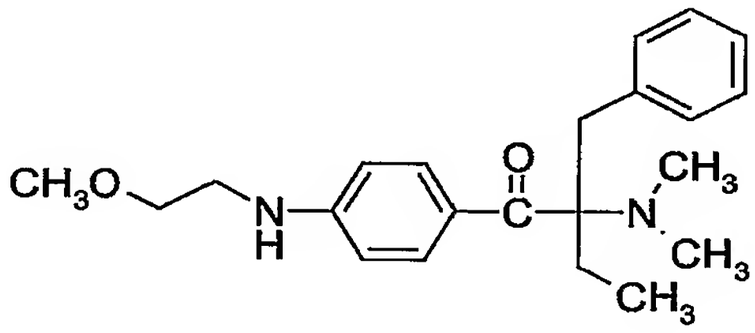
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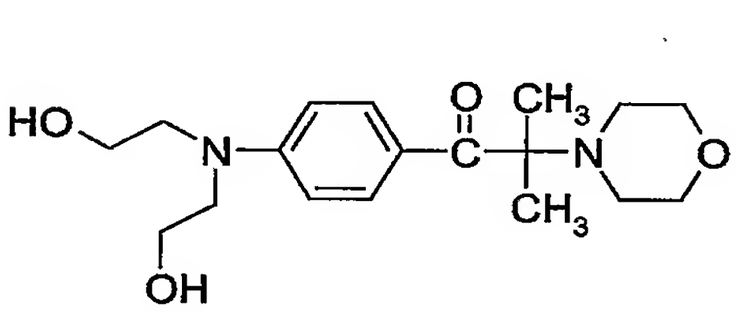
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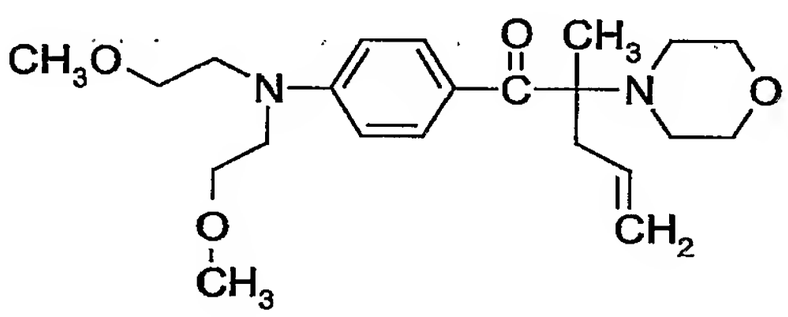
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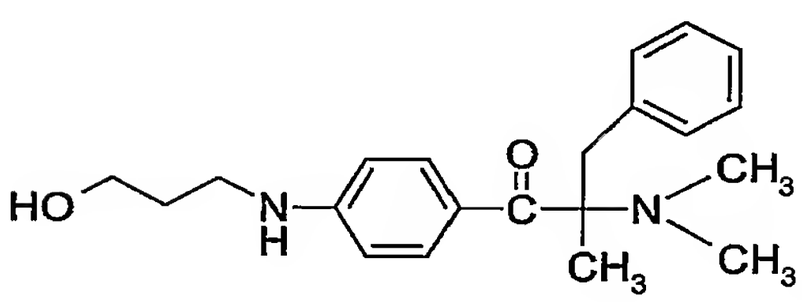
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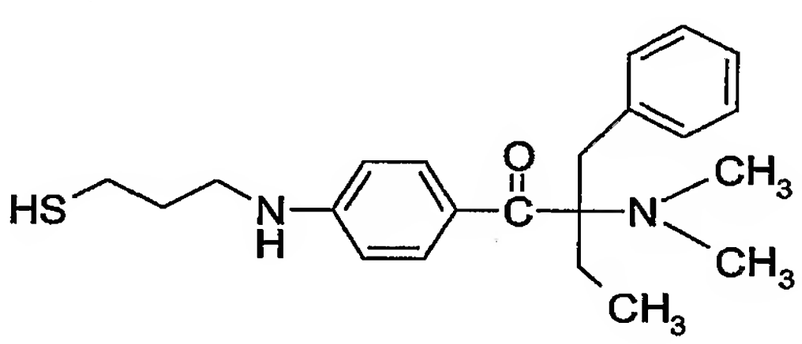
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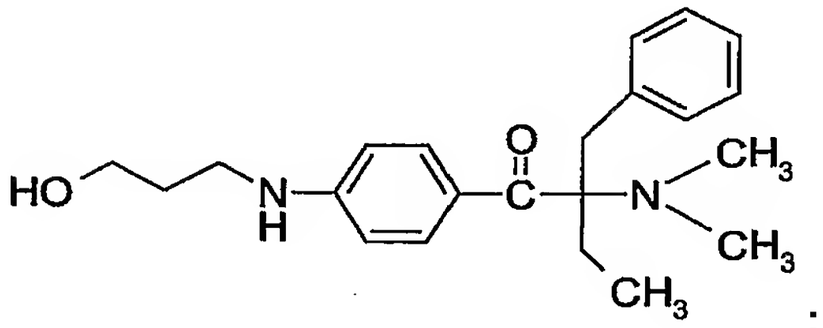
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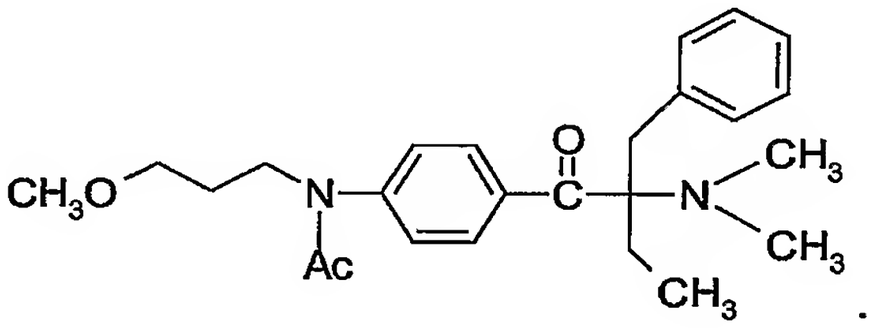
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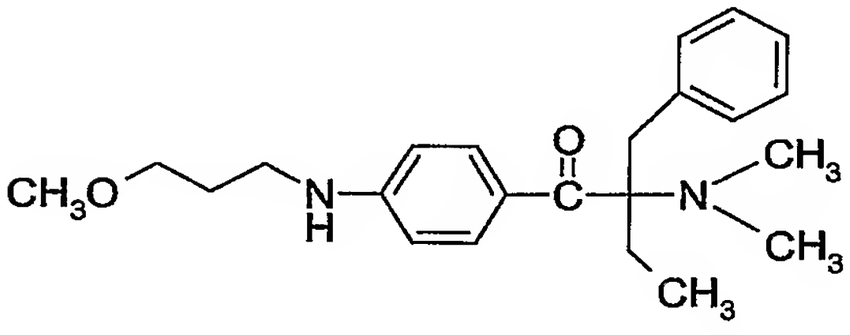
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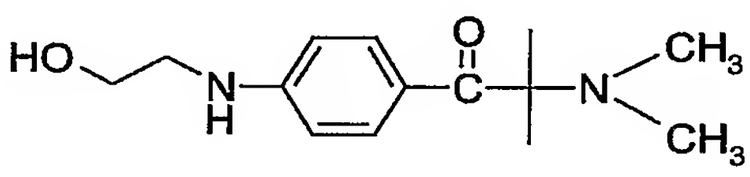
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2. Photoinitiators according to claim 1, wherein

n is 1 or 2;

L is a linker;

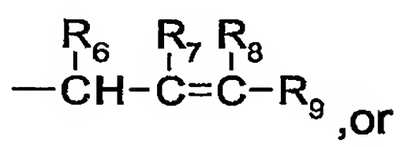
X is –O-, -S- or –NR_{32}-;

Z is a direct bond;

R_1 is

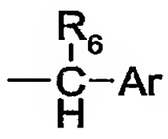
(a) linear or branched unsubstituted C_1-C_{12}-alkyl;

(b) a radical of the formula;



,or

(d) a radical of the formula



wherein Ar is phenyl, which is unsubstituted or substituted by one or more of the groups NO_2, -$N(R_{10})_2$, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylthio, phenoxy;

R_2 if n is 1, independently of R_1 has one of the meanings of R_1;

R_2 if n is 2, is C_2-C_8alkylene;

R_3 is C_1-C_4-alkyl, C_2-C_4-alkyl substituted by hydroxy, C_1-C_4-alkoxy; C_3-C_5-alkenyl;

R_4 independently of R_3 has one of the meanings of R_3; or R_4 together with R_3 is C_4-C_5-alkylene that may be interrupted by -O-, -$N(R_{13})$-;

R_5 is hydrogen;

R_6, R_7, R_8 and R_9 independently of each other are hydrogen or methyl;

R_{10} is hydrogen, C_1-C_4-alkyl or C_3-C_5-alkenyl;

R_{13} is hydrogen or C_1-C_4-alkyl;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{12}-alkyl; or C_2-C_6-alkyl substituted by hydroxy, C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or -COO(C_1-C_4-alkyl); allyl, cyclohexyl or C_7-C_9-phenylalkyl; or C_2-C_{12}-alkanoyl, benzoyl or norbornenoyl; or C_2-C_{12}-alkanoyl, benzoyl or norbornenoyl substituted by C_1-C_4-alkoxy, -COOH or -COO(C_1-C_4-alkyl); or C_3-C_5-alkenoyl; or -CO-NH-C_1-C_{12}-alkyl or –CO-NH-(C_0-C_{12}-alkylen)-N=C=O, optionally interrupted by one or two phenylene,methylphenylene, phenylene-O-phenylene, cyclohexanediyl, methylcyclohexanediyl, trimethylcyclohexanediyl, norbornanediyl, [1-3]diazetidine-2,4-dione-1,3-diyl, 3-(6-

isocyanatohexyl)-biuret-1,5-diyl or 5-(6-Isocyanatohexyl)-[1,3,5]triazinane-2,4,6-trione-1,3-diyl;

R_{32} is hydrogen or C_1-C_{12}-alkyl.

3. Photoinitiators according to claim 2, wherein

n is 1 or 2;

L is linear or branched C_2-C_{18}-alkanediyl;

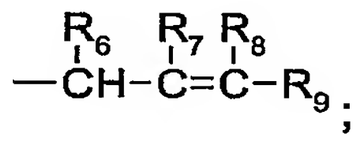
X is –O-;

Z is a direct bond;

R_1 is

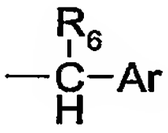
(a) linear or branched unsubstituted C_1-C_3-alkyl;

(b) a radical of the formula;



;

(d) a radical of the formula



where Ar is phenyl, which is unsubstituted or substituted by CH_3-NO_2 or -$N(R_{10})_2$;

R_2 if n is 1, independently of R_1 has one of the meanings of R_1;

R_2 if n is 2, is C_2-C_8alkylene;

R_3 is methyl,

R_4 is methyl or R_4 together with R_3 is C_5-alkylene that is interrupted by -O-;

R_5 is hydrogen;

R_6, R_7, R_8 and R_9 are hydrogen;

R_{10} is hydrogen;

R_{30} and R_{31} independently of one another are hydrogen, C_1-C_{12}-alkyl; or C_2-C_6-alkyl substituted by hydroxy; C_1-C_4-alkoxy, -O-CO-(C_1-C_4-alkyl), or C_3-C_5-alkenoyl.

4. Photoinitiators according to any one of claims 1-3, wherein n is 1 or 2, R_1 is benzyl, 4-aminobenzyl, propyl or allyl and R_2 is ethyl or is C_2-C_8alkylene.

5. A composition comprising

(A) at least one ethylenically unsaturated compound;

(B) a photoinitiator of formula I as defined in claim 1.

6. The use of compounds of the formula I as defined in claim 1 as photoinitiators to cure compositions according to claim 5.

7. The use of compounds of the formula I as defined in claim 1 to prepare multifunctional photoinitiators: